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Dilute Magnetic Semiconductors

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We present first principles calculations for prospective magnetic materials for future applications in spintronics. Spintronics combine the charge and spin degree of freedom of the electrons making it possible to create novel devices with increased functionality compared to semiconductor devices used today. The material studied is focused on dilute magnetic semiconductors (DMS) like $Ga_{1-x}Mn_xAs$ that play a key role in semiconductor spintronics. Due to their ferromagnetic properties they can be used in magnetic sensors and as spin injectors. The basic problem for applications are, however, the relatively low Curie temperatures of these systems. We therefore focus on understanding the magnetic properties and on a reliable calculation of Curie temperatures from first principles. We have developed a theoretical framework for calculating critical temperatures by combining first principles calculations and statistical methods like Monte Carlo simulations.

1 Introduction

Magnetic materials have been known to mankind for a very long time. Perhaps the most famous example is the compass needle but today magnets are used everywhere, as permanent magnets in electrical motors in our cars, in harddrives on our computers and mp3-players, in loadspeakers, credit cards etc. Meanwhile, semiconductor based devices that use the charge of the individual electrons as the information carrier, have extensively been used in the last century in integrated devices like microprocessors, memory modules and diodes used in computers, amplifiers, cell phones etc. The performance of these devices has increased by several orders of magnitude over the last decades (according to Moore's law, the performance on transistors double every 18 mounts). This performance gain is due to, among other things, development in manufacturing and fabrication which makes it possible to shrink the dimension of the transistors and pack them more densely in order to make a faster device which simultaneously runs cooler and more efficiently. However, nowadays this route to improve performance seems to face severe difficulties, because the dimensions are becoming so tiny that classical physics no longer is applicable and quantum effects start to become important, like tunneling through the gate oxide layer causing malfunction of the transistor. Of course, this has been known for a long time and so far the industry has all the time found new clever ways to overcome the problem and make the devices go faster. For instance, Intel replaced the gate oxide from silicon dioxide to a rare earth based material (hafnium silicide) in their latest 45nm process, which improves not only the switching speed of the transistor but also reduces the power needed. However, all this development *will* eventually come to an end where it is simply not possible to shrink the dimensions further. It is here *spintronics* enter. The basic idea is to make devices where quantum mechanics is actually employed and not fought against. The electrons not only carry electrical charge but also spin, a purely (relativistic) quantum effect that can not be explained by classical physics. The spin is then manipulated in the spintronic device,

instead of the charge, schematically shown in Figure 1.

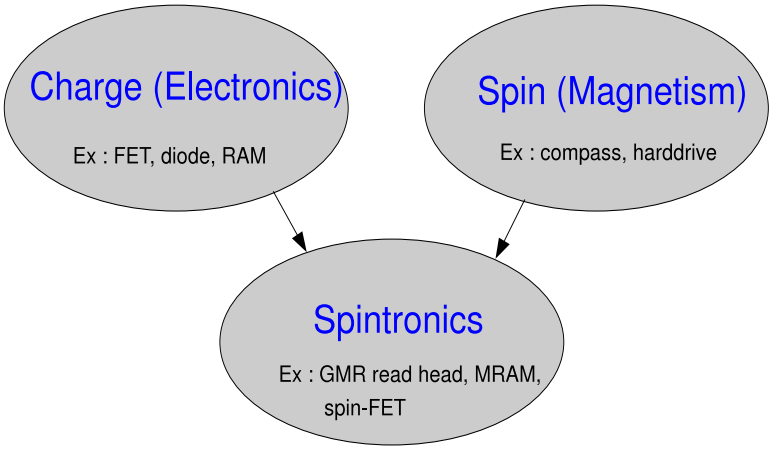

Figure 1. Schematic overview of spintronics which combines both charge (electronics) and spin (magnetism) into a novel field of research and applications.

The most successful application of spintronics to date is without any doubt the giant magneto resistance (GMR) read head in harddrives, an effect that was discovered by P. Grünberg and A. Fert who received the 2007 Nobel Prize in Physics. In very simple terms, the effect arises in a multilayer that consists of alternative magnetic and nonmagnetic materials in which the electrical resistivity depends on the magnetic configuration of the magnetic layers.

Dilute magnetic semiconductors like $Ga_{1-x}Mn_xAs$ are considered as ideal materials for spintronics. Only a few percent of Mn impurities are needed to achieve ferromagnetism. Thus the hope is that they can substitute the metallic ferromagnets to achieve all-semiconductor spintronics. Moreover they are half-metallic exhibiting a 100% spin polarization at the Fermi level E_F, being ideal for spin dependent devices. Their biggest disadvantage is that the reported Curie temperatures are well below room temperature. Here we will present some results of *ab initio* calculations, showing the complexity of these systems.

2 Computational Methods

The main goal of this study is to calculate critical temperatures T_c of several DMS systems. For applications the T_c needs to exceed room temperature by some margin since it determines in a way the upper working temperature of the device. To calculate T_c for realistic systems using only quantum mechanics methods is a formidable task which has not yet been solved. We have therefore used an alternative approach where we have split the problem into two parts, here called a two-step approach. In the first step, we apply quantum mechanical calculations using density functional theory to calculate the total energy of the system. These calculations do not have any adjustable parameters nor need

input from experiments. The total energy is then mapped to a simplified solvable model, in this case a classical Heisenberg model, which we solve in the second step by applying statistical methods to estimate T_c. Although simplified, this is by no means simple and in order to obtain reliable results, large scale calculations are called for.

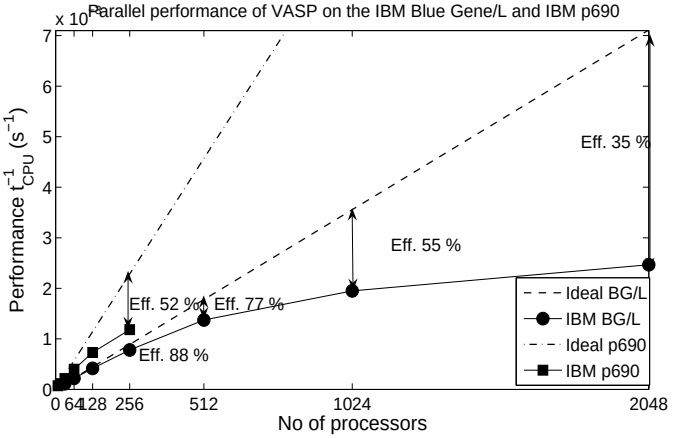

Figure 2. Parallel performance of VASP on the IBM p690 cluster (JUMP) and the IBM Blue Gene/L (JUBL) at the Research Centre Jülich.

The quantum mechanical calculations are based on density functional theory (DFT) in combination with the local spin density approximation (LSDA). These calculations are able to predict many physical quantities of real materials using only the lattice geometry and atomic numbers as input parameters. In practice, many different implementations exist based on various degrees of sophistication. We use the program VASP (Vienna *Ab initio* Simulation Package) of J. Hafner and G. Kresse[1–3] for our studies. VASP is a complete package for performing *ab initio* molecular dynamics (MD) simulations using either pseudopotentials or the projector-augmented wave method (PAW) and a plane wave basis set. The VASP code is spin polarized and fully relativistic and can therefore treat most systems in the periodic table. The program is written in Fortran90 and is massively parallelized using the MPI library. The parallelization is done over the bands and/or over plane wave coefficients to improve scaling. Moreover, the program relies a lot on Fast Fourier Transforms (FFT) which is also done in parallel. From a code optimizing point of view, the code steps through time, and performs a Fast Fourier Transform (FFT) and a matrix diagonalization using iterative routines (RMM-DIIS or blocked Davidson) every time step. The diagonalization is optionally performed using SCALAPACK routines. The VASP program has been ported to both the IBM p690 cluster (JUMP) and to the IBM Blue Gene/L (JUBL) at the Research Centre Jülich.

In Figure 2 we show a scaling plot of the parallel performance of VASP on the JUMP and the JUBL computers. The total number of atoms in the unit cell was 250, which is a typical number for a large-sized problem. The program on JUMP does scale acceptable up to 256 processors with the efficiency above 0.5. Due to the faster interconnect on the Blue Gene/L computer, the program scales much better than on JUMP and show acceptable

scaling of more than 50% up to 1024 processors. Given that each individual processor on JUBL is slower than on JUMP, one needs approximately twice as many processors on JUBL compared to JUMP for the same performance but this is a minor issue due to the larger resources and the relatively good scaling on JUBL. A profiling of the parallel performance on the JUBL reveals that the matrix diagonalizing routines which use the parallel SCALAPACK library do not scale well above 512 processors which hinders a good overall scaling (above 512 procs.). However, it should be said that the most time consuming routine in VASP, which is the iterative matrix diagonalizing routines using the RMM-DIIS algorithm, scales perfectly linearly up to 2048 processors. The memory requirement of VASP is by all means quite large, which has the implication that one usually needs to run the program in coprocessor mode on JUBL. However, the memory requirement per node decreases with increasing number of processors due to data distribution over the nodes. Moreover, with the new Blue Gene/P computer this should be a minor issue due to the larger available memory on that computer.

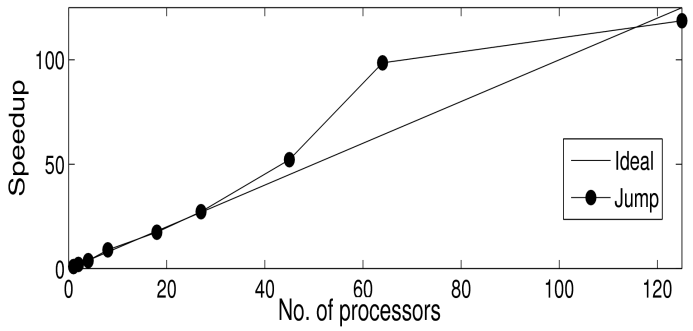

Figure 3. Speedup of parallel MC on the IBM p690 cluster (JUMP) at the Research Centre Jülich.

Once the classical Heisenberg model has been constructed from our first principles calculations, we apply statistical methods to obtain finite temperature properties from the calculated exchange coupling constants. We are using Monte Carlo (MC) simulations for this. MC gives a numerical solution in which both the positional disorder and the spin fluctuations are treated exactly. The simulations are performed on a fixed lattice using the Metropolis or the heat bath algorithm. The fixed lattice allows for fine grained parallelization using domain decomposition of the lattice using MPI which in turn allows for studies on very large simulation cells. Technical details are found in Ref.[4]. Magnetic exchange interactions as far out as 25 shells of neighbours from a central atom can be treated, which is crucial for real metallic systems where the interactions typically are long ranged as well as for diluted systems.

In Figure 3, scaling of the MC program as a function of number of processors on the JUMP computer are displayed. As seen from the figure, excellent scaling, in fact super-

linear scaling for some sizes, are obtained up to 125 processors. The program has a very small memory requirement (a few megabytes) and also run very well on the Blue Gene/L.

3 Diluted Magnetic Semiconductors (DMS)

A diluted magnetic semiconductor (DMS) can be realized by alloying of magnetic elements in a regular semiconductor like GaAs. Some of the Ga cations will then be replaced by magnetic atoms like Mn which carry a local magnetic moment. Moreover, if the valence of the substituted atom is different from the cation, holes are introduced which can mediate (ferro) magnetic interactions between the Mn atoms. An important consequence of this substitution is that the magnetic atoms are diluted and have a random distribution. DMS like $Ga_{1-x}Mn_xAs$ are one of the most hopeful materials for an all semiconductor spintronics. An enormous amount of papers and strong progress has been produced in this field, but the bottleneck for applications is still the availability of DMS with Curie temperature T_c above room temperatures. Thus understanding, predicting and realizing DMS with T_c larger than room temperature is one of the most important problems in spintronics. The highest conclusively reported T_c of DMS is around 170 K for 8% Mn doped GaAs, which is too low for applications.

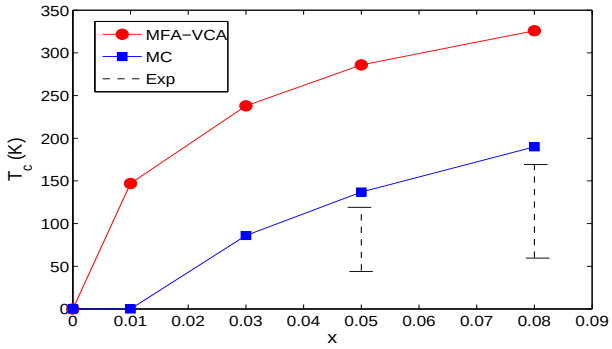

Figure 4. Calculated Curie temperatures of Mn-doped GaAs as a function of Mn concentration x using the mean field approximation (MFA-VCA) and Monte Carlo simulations (MC). The exchange coupling parameters are calculated from LDA.

Over the years, more and more knowledge has been gathered on DMS systems. For example, it has been demonstrated that electron doping strongly reduces the ferromagnetism leading to a disordered local moment state (DLM)[5]. The dominating exchange mechanism leading to ferromagnetic order, i.e. Zeners's $p-d$-exchange and Zener's double exchange, have been clarified by *ab initio* calculations and are now well understood[6,7]. Moreover, it has been demonstrated that percolation and disorder effects play a crucial role in these system by strongly reducing the ferromagnetism[8–10]. As an example, in Figure 4 calculated Curie temperature of Mn-doped GaAs is displayed as a function of concentration of substituted Mn-atoms employing the LDA. The most accurate method, namely MC simulations, yields T_c values that due to percolation problems are considerably lower than

previous mean field estimates (MFA-VCA), e.g. by Dietl *et. al.*, so that percolation seems to present a general obstacle for high T_c in DMS. This is particularly true for DMS like (Ga,Mn)N or (Zn,Cr)Te, in which due to the wide band gap the interaction is very short ranged. However, even for (Ga,Mn)As, where the interaction is fairly long ranged, this is a significant effect (see Figure 6).

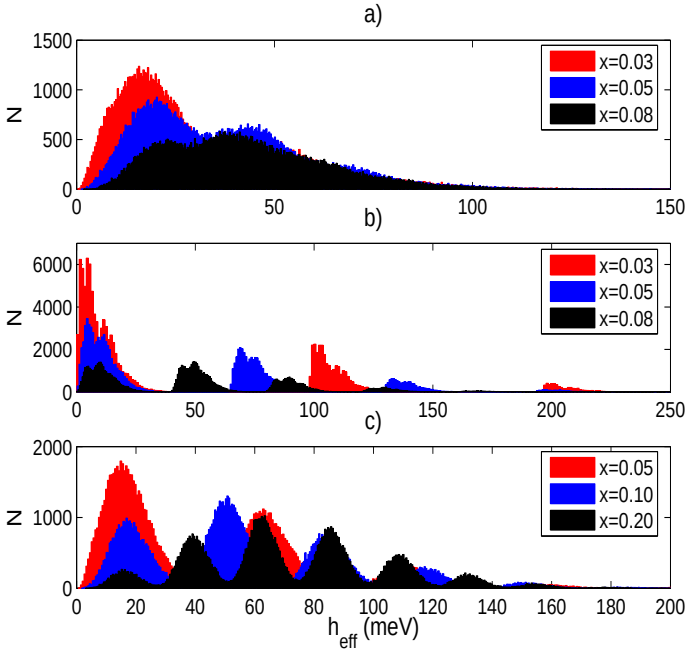

Figure 5. Distributions of local magnetic fields for a) Mn-doped GaAs, b) Mn-doped GaN and c) Cr-doped ZnTe. x denotes the concentration of magnetic impurities.

In order to get a more complete picture why the mean field approximation together with the virtual approximation (MFA-VCA) sometimes completely fails, but at other times gives reasonable results we have performed an analysis of the local effective magnetic fields h^{eff} in DMS materials. To be more specific, the h^{eff} is defined as

$$h_i^{\text{eff}} = \sum_j J_{0j} \langle S_j^z \rangle, \tag{1}$$

for each magnetic site i and at $T = 0K$, $\langle S_j^z \rangle = 1$. In a non-random system, each site i has the same value of h^{eff}. However, in contrast, in random system like DMS each site has a different local environment and we will instead obtain a distribution of local effective magnetic fields as displayed in Figure 5 for Mn-doped GaAs, Mn-doped GaN and Cr-doped ZnTe. The distribution is obtained for huge systems with around 10^5 magnetic impurities to make sure that basically all local environments are included. If a deeper analysis is performed, one can conclude that the MFA-VCA method is reasonable if the distribution is close to a Gaussian. If not, then the MFA-VCA method will fail spectacularly.

The distribution for Mn-doped GaAs (Figure 5a) does not differ dramatically from a Gaussian, especially for the higher concentrations. Consequently, of the three different DMS systems considered here it is the system where the MFA-VCA estimate is closest to the exact MC value (approximately a factor of 2 too large). The situation in GaN is very different (Figure 5b). The distribution is very far from a Gaussian but instead it consists of several peaks (arising from the dominant interactions in the 110-direction). It is clear from this distribution that the MFA-VCA estimate will be very wrong and this is indeed the case (the exact MC values are about one order of magnitude lower). An intermediate case is Cr-doped ZnTe, in which the distribution shows several smaller peaks. On the other hand, the concentration of magnetic atoms is larger than in the two cases above making the MFA-VCA estimate slightly improved.

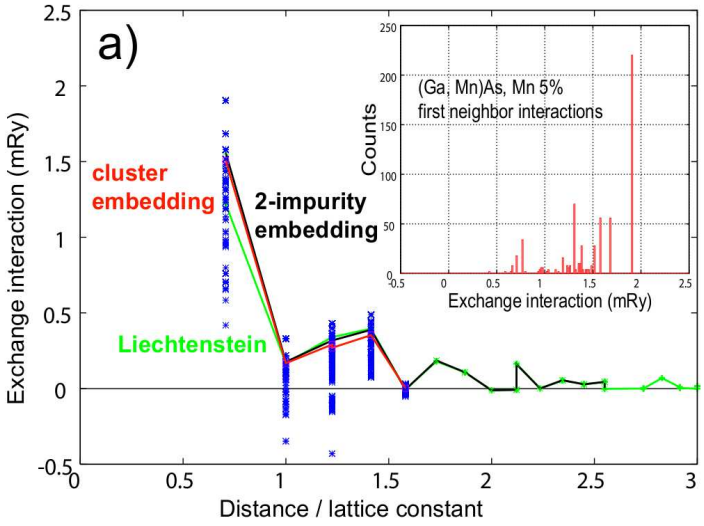

Figure 6. Exchange interactions in 5% Mn-doped GaAs using cluster embedding in CPA medium as a function of distance. The inset shows the distribution of nearest neighbour interaction.

Another important question is: How well can the exchange coupling constants J_{ij} between two impurities at sites i and j be described by a unique value J_{ij} independent of the local environments, i.e. the location of other magnetic impurities in the vicinity of the (i, j) pair? In the standard approach by Lichtenstein this effect is thought to be included by using averaged Green's functions based on the coherent potential approximation (CPA). We have investigated his problem in detail by calculating J_{ij} for a series of disordered local environments (clusters) embedded in the CPA medium. The results presented in Figure 6 show large fluctuations of the J_{ij} data, depending strongly of the positions of third and fourth Mn impurities in the neighbourhood of i and j. The inset shows the frequency distribution of nearest neighbour values J_{01}. The configurational average is in disagreement with the Lichtenstein's results based on the CPA, at least for the nearest

neighbour interactions. However, it agrees well with the exact results for two impurities i and j embedded in the CPA medium, showing that the disorder is well described by the CPA, provided that the 2-impurity problem is solved correctly.

4 Concluding Remarks

We have presented a theoretical investigation of prospective materials for future applications in spintronics, namely diluted magnetic semiconductors, using a combination of quantum mechanical calculations and statistical methods. Unfortunately, the critical temperatures are still too low for practical use.

Acknowledgments

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